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This is the Published version of the following publication

Gray, Stephen R, Ritchie, C. B, Tran, Thuy and Bolto, Brian (2007) The effect of NOM characteristics and membrane type on microfiltration performance. *Water Research : a Journal of the International Water Association (IWA)*, 41 (17). 3833 -3841. ISSN 0043-1354

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The effect of NOM characteristics and membrane type on microfiltration performance

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Abstract

Efforts to understand and predict the role of different organic fractions in the fouling of low-pressure membranes are presented. Preliminary experiments with an experimental apparatus that incorporates automatic backwashing and filtration over several days has shown that microfiltration of the hydrophilic fractions leads to rapid flux decline and the formation of a cake or gel layer, while the hydrophobic fractions show a steady flux decline and no obvious formation of a gel or cake layer. The addition of calcium to the weakly hydrophobic acid (WHA) fraction led to the formation of a gel layer from associations between components of the WHA. The dominant foulants were found to be the neutral and charged hydrophilic compounds, with hydrophobic and small pore size membranes being the most readily fouled. The findings suggest that surface analyses such as FTIR will preferentially identify hydrophilic compounds as the main foulants, as these components form a gel layer on the surface while the hydrophobic compounds adsorb within the membrane pores. Furthermore, coagulation pre-treatment is also likely to reduce fouling by reducing pore constriction rather than the formation of a gel layer, as coagulants remove the hydrophobic compounds to a large extent and very little of the hydrophilic neutral components.

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Keywords: Microfiltration; Membranes; Natural organic matter; Fouling

1. Introduction

Many factors affect membrane fouling by natural organic matter (NOM), including the nature of the NOM (size, hydrophobicity, charge), the membrane (hydrophobicity, charge, surface roughness), the solution (pH, ionic strength, hardness ion concentration) and the hydrodynamics of the membrane system (solution flux, surface shear) (Taniguchi *et al.* 2003). In a study of hollow fibre microfiltration (MF) membranes treating two surface water sources (Gray *et al.* 2007), we have explored varying solution conditions such as NOM concentration, the ionic strength and the pH level, as well as the improvement gained by prior alum treatment, a topic that has been reviewed recently (Farahbakhsh *et al.* 2004). The current paper is devoted to the influence of various NOM fractions on membrane performance, so that a better understanding of the mechanism of NOM fouling might be obtained.

The use of NOM fractions from Moorabool River, near Anakie in south eastern Australia to test which types of compounds are responsible for MF membrane fouling revealed that for a polypropylene (PP) hollow fibre system, the neutral hydrophilic fraction was the most strongly implicated (Carroll *et al.* 2000). There was a 40% decrease in flux after a throughput that caused only a 20% decrease for the other fractions – the strongly and weakly hydrophobic acids and charged hydrophilic material. The three less-fouling fractions had their DOC reduced by 48, 49 and 64% respectively following alum treatment, while there was no DOC removal for the neutral hydrophilic fraction. Prior treatment with alum significantly reduced the rate of fouling by the raw water (by a 50% decrease versus 82% for the untreated raw water). Alum treatment had only a small influence on the fouling rate despite substantial removal of the charged fractions, the fouling by the neutral hydrophilic fraction being just slightly less than for alum-treated raw water (Carroll *et*

51 *al*, 2000). It is likely that the alum treated water still contained the neutral fraction, as Tran *et al*
52 (2006) has shown coagulation to remove the neutral hydrophilic fraction only slightly, while the
53 other fractions were removed to a far greater extent.

54
55 Other experiments on hydrophobic and hydrophilic MF membranes gave fouling potentials by NOM
56 from surface waters as neutral hydrophilic fraction > strongly hydrophobic acids > weakly
57 hydrophobic acids > charged hydrophilic fraction (Fan *et al.* 2001). The fouling rate for the
58 hydrophobic membrane was considerably greater than for the hydrophilic membrane. In the
59 fractionation process it was found that calcium became concentrated in the neutral fraction,
60 suggesting that organic/ Ca^{++} complexes were formed that could become bound to the negatively
61 charged membranes. Pre-filtration of the neutral hydrophilic fraction with a 30 kDa UF membrane
62 significantly reduced fouling rate. Most of the neutral compounds in the neutral hydrophilic fraction
63 were of low MW, showing that it was only the small amount of high MW matter that were the
64 strongest fouling components.

65
66 A small component of the total NOM was also found to be responsible for the major fouling of MF
67 membranes in another study (Howe and Clarke 2002). NOM in natural water samples was
68 fractionated with UF membranes to obtain various MW fractions. The major fouling effect occurred
69 with compounds larger than 3 nm, which corresponded to only 10-15% of the total NOM.
70 Furthermore, marked differences in the extent of fouling between membranes of similar pore size
71 but different composition were observed, leading to the conclusion that adsorption of NOM was the
72 mechanism that led to MF fouling.

73
74 Aquatic NOM fractions have been passed through a hydrophobic polypropylene MF membrane and
75 the flux decline monitored (Gray *et al.* 2004). The fraction containing all the hydrophobic acids
76 fouled the membrane more than the individual strongly hydrophobic acid and weakly hydrophobic

acid fractions, suggesting that association between the latter two entities may be occurring to cause the more severe fouling effect. Such interactions have been proposed for similarly charged polyelectrolyte/fatty acid monolayer systems (Gole *et al.* 2003) and for hydrophobically-modified anionic polyelectrolytes and anionic surfactants (Deo *et al.* 2003). Much more work has been carried out on ultrafiltration (UF) and nanofiltration (NF) systems, some of which is summarised in Table 1.

In a study encompassing several membrane types, the present paper is aimed at understanding the fouling mechanism of each NOM fraction on membranes of varying composition, and when additional salt is added.

2. Experimental

2.1 Water Source

Reverse osmosis with a 5 µm pre-filter was used to concentrate NOM in water from Lake Eppalock, Bendigo, that had TOC 7.9 mg/L, UV₂₅₄ 0.182 cm⁻¹ and SUVA₂₅₄ 2.30 L/mg.m. Likewise a concentrate NOM was obtained from the Moorabool River at Anakie. The raw water had TOC 9.1 mg/L, UV₂₅₄ 0.154 cm⁻¹ and SUVA₂₅₄ 1.69 L/mg.m. The use of RO to concentrate NOM from fresh waters has been recommended because of the very high percentage of NOM recovered and the rapidity of the process (Serkiz and Perdue, 1990). NOM recovery has been estimated in terms of colour removal as 80-100%, and in terms of permanganate oxidation, 50-99% (Ødegaard and Koottatep, 1982). Other workers quote NOM recovery by RO up to 99.7% (Schäfer, 2001). One study has shown that RO isolates have a higher MW than the original raw filtered water, leading to the postulation that some condensation reactions may occur during the isolation process (Maurice *et al.*, 2002). However, a detailed study found that properties such as size,

polarity, charge density and isoelectric point were preserved with RO isolation, which gave an organics rejection of >99% (Kilduff *et al.*, 2004).

Two methods, variations of the published procedure (Carroll *et al.* 2000), were used to isolate different components from the NOM. Procedure A is identical to the fraction procedure used before except that it further divides the hydrophilic neutral fraction into two sub-fractions: hydrophobic bases (HB) and residual hydrophilics (Res).

A portion of the neutral hydrophilic fraction was retained from procedure A so that it could be compared to its sub-fractions. The other four fractions were: a strongly hydrophobic acids (SHA) fraction separated on Supelite DAX-8 at pH 2; a weakly hydrophobic acids (WHA) fraction separated on Amberlite XAD-4 at pH 2; a hydrophilic charged fraction (Char) of anionic material separated on Amberlite IRA-958 at pH 8; and a hydrophilic neutral fraction (Neut) which does not adsorb on any of the above. The hydrophobic bases were removed from the neutral hydrophilic fraction by adsorption on Supelite DAX-8 at pH 8, while the residual hydrophilics were not adsorbed on the Supelite DAX resin. Fractionation procedure B did not use the DAX 8 resin to isolate NOM, and all hydrophobic compounds were removed on the XAD 4 resin as hydrophobic acids (HA) (Gray *et al.* 2004).

The NOM fractions were removed from the DAX-8 and XAD-4 resins by elution with NaOH for the hydrophobic acids (SHA, WHA and HA) and by elution with HCl for the hydrophobic bases. The Char components were eluted from the Amberlite IRA-958 by acidic NaCl solution. Once eluted, NOM was de-salted by use of ultra-filtration.

The make up of the NOM is shown in Table 2. Meredith water was much higher in the SHA fraction at the expense of the WHA material; otherwise the compositions were rather similar.

128

129 Evidence from solid state ^{13}C nuclear magnetic resonance spectra (Wong *et al.*, 2002) has previously
130 shown the hydrophobic fractions to be high in aliphatic and aromatic carbon, while the weakly
131 hydrophobic organics have more carbonyl and alkoxy carbon. Hydrophilic fractions show strong
132 alkoxy signals attributable to carbohydrates, while for one water phenolic carbon was present.
133 Generally, the SHA is considered to contain predominantly humic acids, WHA predominantly fulvic
134 acids, Char predominantly fatty acids and carbohydrates and the neutral hydrophilics predominantly
135 carbohydrates and polysaccharides. However, all fractions undoubtedly contain a mixture of the many
136 compound types present in the original water (Owen *et al.*, 1993).

137

138 The relative concentrations of colloidal NOM were characterized by liquid chromatography using an
139 organic carbon detector (LC-DOC) at Curtin University. The Meredith water was shown to have
140 approximately twice as much colloidal NOM as the Bendigo water, although the absolute concentrations
141 could not be determined. It was assumed that this component of NOM reports predominantly to the
142 hydrophilic fraction of NOM as it is composed of polysaccharide based material (Croué, 2004). This is
143 consistent with the previous NMR analysis of NOM (Wong *et al.*, 2002).

144

145 2.2 Membranes

146 A single hollow fibre membrane filtration rig was used to examine the fouling characteristics of
147 each NOM fraction, using the previously described procedure (Gray *et al.* 2004). The filtration
148 apparatus allowed the filtration to be performed at a constant pressure of 0.5 bar and the membranes
149 to be backwashed every 30 minutes using a liquid backwash (0.8 bar). The filtration results are
150 presented as a relative flux (membrane flux at 20°C/flux with Milli Q water at 20°C) versus
151 filtration throughput when presented in graphical form, or in tabular form as a relative flux after a
152 given mass of filtrate had passed. The extent of flux recovery upon backwashing could be estimated

from the change in relative flux following backwashing (or the width of the line in the relative flux versus filtrate graph).

The membranes used were three Memcor products, a hydrophobic polypropylene (PP) membrane with a nominal pore size of 0.2 μm and contact angle of 160° , and hydrophobic (PVDF-1; contact angle 115°) and hydrophilic (PVDF-2; contact angle of 61°) polyvinylidene fluoride membranes, which had nominal pore sizes of 0.1 μm respectively. A poly(ether sulphone) membrane from Thames (PES-2) having a nominal pore size of 0.01 μm and a contact angle of 59° was tested also. All filtration experiments were conducted at pH 6, and the DOC concentrations were held constant for each water (ie. Bendigo or Meredith).

Following the filtration experiments, the microstructures of the PP membrane surfaces were characterised using a Philips XL30 field emission scanning electron microscope (SEM) in both the secondary and back-scattered electrons (BSE) modes operating at 5-15kV. Associated energy-dispersive X-ray spectroscopy (EDS) was also used to obtain chemical information.

3. Results and Discussion

3.1 NOM Fractions

Experiments on MF of the NOM fractions were carried out using the four membranes described above. The effects on flux and throughput were explored. Results for the PP membrane are given in Fig. 1 and 2. It can be seen that the greatest flux decline occurs with the Neut fraction for both Bendigo and Meredith NOM, the next most potent foulants being the Char fraction, followed by the least fouling SHA and WHA fractions. Figures 3 and 4 show SEM photographs of the fresh PP membrane surface and the PP surface following filtration with raw water. Comparison of these two figures shows that filtration of the raw water leads to the formation of a gel layer on the surface.

180 The fouling caused by the hydrophobic fractions (SHA and WHA) may be attributed to the
181 adsorption of the hydrophobic acids on the hydrophobic PP membrane. The flux recovery on
182 backwashing is small compared to the Char and Neut fractions (width of lines in Figures 1 and 2)
183 and the SEM photographs following filtration with the WHA fraction has little surface fouling
184 evident (Figure 5). These results are consistent with fouling via pore constriction.

185

186 In comparison, the flux decline curves for the Char and Neut fractions may be attributed to the
187 formation of a cake or gel layer on the membrane surface. There is greater flux recovery upon
188 backwashing for these fractions and the SEM photograph following filtration by the Char fraction
189 (Figure 6) shows the presence of a gel layer.

190

191 Table 3 shows the Bendigo flux results for all membranes after 3 L throughput of the raw water and
192 its various NOM fractions. It is apparent generally that the Neut and HB fractions have the greatest
193 effect on flux, and WHA the least. There was only enough HB material to test on the one membrane
194 and the results were identical to those for the Neut fraction. The formation of the gel layer on the
195 surface of the membrane by the Neut and Char fractions appears to lead to faster flux decline for
196 these waters than pore constriction from the SHA and WHA fractions. The formation of the gel
197 layer on the membrane surface might be regarded as being the result of filtering large particles or
198 organic complexes that are too large to be filtered. While this may be possible, and the presence of
199 large entities in the cake layer will lead to a faster formation of this layer, previous work has also
200 shown that the flux decline of MF and UF membranes does not alter when the permeate is re-filtered
201 through another clean membrane (Makdissy *et al.* 2004). If the cake layer were the result of entities
202 that were too large to pass through the membrane, then these entities should be removed and
203 re-filtering the permeate should lead to a lower flux decline. However, the fact that similar flux
204 declines have been observed when the permeate has been re-filtered suggests that the cake layer may

be formed on the surface by associations between organic compounds. Given the gel layer appeared for the Char and Neut fractions of NOM it is evident that the gel layer is the result of filtering polysaccharide material rather than humic substances.

Combining the SHA and WHA fractions (1:1; no salt addition) before passing them through the PES-2 membrane resulted in a greater flux decline than either of the two separate fractions, with nearly a halving of the flux at low throughputs. Pore blocking by what seem to be larger species may be occurring. There was little difference in behaviour with the two PVDF membranes. If there is association or clustering of the two hydrophobic fractions, it might be expected to have more influence on the less polar membranes, which is observed to a small extent for the PP membrane, but not for PVDF-1. These results re-enforce the proposition that the hydrophobic compounds do not by themselves lead to the formation of a cake or gel layer except perhaps for the smaller pore size UF membranes.

The effect of the various Meredith NOM fractions on membrane behaviour is shown in Table 4. With the PP membrane the Char fraction has the greatest effect on flux, and the hydrophobic fractions the least, whereas for the PVDF-2 membrane the Char fraction fouls insignificantly. This is due to the greater flux recovery upon backwashing for the PVDF membrane compared to the PP membrane (see Figure 7 for a typical comparison of flux recoveries between PP and PVDF membranes) when the Char fraction is filtered, and re-enforces the notion that the adhesion between the membrane and the gel layer is critical in determining the rate of flux decline.

The most severe flux decline for the PP membrane was with the Char and Neut fractions. For the PVDF-2 membrane the Neut fraction was again the worst offender, similar to the raw water. The Char, SHA and WHA fractions are much less fouling, and HA the least.

The addition of salt to raw Meredith water and its NOM fractions had pronounced effects in some cases, as also shown in Table 4. For the hydrophobic PP membrane there was a dramatic reduction in flux for the WHA compounds, a similar effect but in the reverse direction for the Char fraction, a slight reduction in flux for the HA fraction and a negligible change for the raw water, SHA and Neut fractions. However for the Type B Neut fraction salt enhanced the flux markedly. Interactions that could account for the PP membrane results may involve calcium ion binding the WHA to the membrane. The presence of calcium, here at only 0.05 mM concentration, has been observed at 1 mM concentration to decrease the size of soil-derived NOM from 300 nm to ~100 nm, but at higher calcium levels a size increase was observed that was ascribed to chelation between the species, although a concentration of >2 mM was required (Xi *et al.* 2004). In the present work a flux reduction at low calcium levels may result from calcium linking the WHA molecules to the membrane, which is not happening to the same extent with the SHA fraction, a fact that could be ascribed to the much greater content of carboxylic acid groups in the WHA molecules, estimated to be some 2.5 times for a French river NOM (Garnier *et al.* 2004). This proposed mechanism is also consistent with the formation of a gel layer with the WHA when the additional salt (NaCl and CaCl₂) are added, as is shown in Figure 8. An analogous explanation has been proposed for an NOM surrogate in the form of a carboxylated latex particle, where it been shown that calcium ions greatly enhanced fouling of a thin film composite membrane made from a semi-aromatic piperazine based polyamide (Li and Elimelech 2004). The calcium ions complex to carboxylic acid groups on the solution NOM and the NOM deposited on the membrane, to form bridges between the two surfaces.

The Char fraction is probably made up of polysaccharide and protein fragments that will contain negative and in the latter case positive sites that can interact electrostatically, providing bonds between molecules. Adding salt will shield the charges and result in disaggregation, giving smaller molecules and a greater flux. Increased ionic strength results in a strong improvement in flux with

the Type B Neut fraction. This fraction also contains hydrophobic basic compounds, and adsorption of these compounds on the membrane, possibly initially by hydrophobic bonding of the basic moiety to hydrophobic patches on the membrane surface, will be more pronounced at the higher ionic strengths. The resulting increased hydrophilicity of the membrane as a result of adsorbing these compounds may be responsible for the higher flux. The effect should be more pronounced for the more hydrophobic PP membrane than for PVDF-2, and indeed the former membrane shows the greater flux increase, nearly threefold that for the PP membrane. This sort of surface modification has been achieved by coating membranes with surfactants (Maartens *et al.* 2000). Non-ionic surfactants of the polyethylene oxide type increased the relative fluxes in UF of a natural brown water. Recovery from a flux decline in UF is also documented for distilled water-detergent systems (Bhattacharyya *et al.* 1979), and flux improvements have been obtained for UF of bovine serum albumin through detergent-pretreated regenerated cellulose, polyacrylic and polyamide membranes (Fane *et al.* 1985).

For the hydrophilic and probably more negatively charged PVDF-2 membrane there appears to be minor changes in the opposite direction to that found for the PP membrane and the WHA fraction, suggesting that a disaggregation mechanism may dominate. But for the Char fraction there is a pronounced effect in the opposite direction, with salt encouraging flux decline. It could be that the greater negative charge on the membrane is enhancing calcium ion binding of the anionic species to the membrane. As with the PP membrane, the Type B Neut fraction enhances flow because of the increased hydrophilicity of the membrane, as organics adsorption is again strong.

The different fouling mechanisms between the hydrophobic and hydrophilic compounds may explain why polysaccharides, proteins and carbohydrates are usually found to be the cause of fouling when FTIR is used to identify the composition of surface coatings. The results from this work indicate that hydrophobic compounds foul by blocking the internal pores of the membrane

while the hydrophilic compounds form surface layers. As FTIR only analyses the surface coatings, only the hydrophilic compounds will be detected, as the hydrophobic compounds are likely to be adsorbed within the membrane pores. Given the poor rejection of NOM by MF, the gel layers that form on the membrane surface are unlikely to reject hydrophobic compounds, so they would be available for adsorption and fouling within the membrane pores even when once the gel layer has formed.

Furthermore, coagulation is known to preferentially remove the hydrophobic and charged compounds and to remove very little of the hydrophilic neutral compounds (Tran *et al*, 2006). Therefore, coagulation prior to MF acts to reduce pore blocking from the hydrophobic compounds, but will have little effect on the formation of a gel layer resulting from the filtration of the hydrophilic neutral components.

4. Conclusions

Hydrophobic membranes fouled more readily than hydrophilic membranes, as did those of small pore size. The most potent foulants were the neutral and charged hydrophilic compounds, as they formed a gel layer on the membrane surface. The SHA compounds were next, then the WHA compounds, neither of which formed cake or gel layers on the surface. Interactions between hydrophobic components may be occurring in some instances, where the level of strongly hydrophobic compounds is high, while the addition of calcium to the WHA fraction led to the formation of a gel layer through associations between the WHA components.

The different fouling mechanisms between hydrophobic and hydrophilic compounds suggests that FTIR analysis will always identify the hydrophilic compounds as the main fouling compounds. FTIR analyses the composition of the surface layers, and therefore will determine the composition

of the gel layer. This was shown to be formed by the hydrophilic compounds, while the hydrophobic compounds fouled the membrane by adsorption within the pores.

The results also suggest that pre-treatment with coagulation will not prevent the formation of a gel layer but will reduce the level of pore constriction by hydrophobic compounds, as coagulation is known to preferentially remove the hydrophobic and charged compounds.

Acknowledgements

The authors would like to thank the Cooperative Research Centre for Water Quality and Treatment for financial assistance.

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Table 1 Summary of UF and NF membrane performance (hollow fibre systems)

Membrane Type	Membrane Polymer	Organics Source	Main Foulant	Membrane Most Affected	Reference
UF, both hydrophobic and hydrophilic	Various	Suwannee River reference samples	Humic acid > fulvic acid	Hydrophobic and less negatively charged	Jucker and Clark 1994
UF, both hydrophobic, hydrophilic	Polyamide, polyethersulphone (PES), cellulosic	Horsetooth Reservoir, Colorado	Neutral hydrophilic compounds	Hydrophobic	Amy and Cho 1999
UF, both hydrophobic, hydrophilic	PVDF	Three Australian waters	High MW neutral hydrophilics	Hydrophobic	Fan <i>et al.</i> 2001
UF, both hydrophobic, hydrophilic	Polysulphone, regenerated cellulose acetate	Fractionated soil-derived humic acid	ArCO ₂ H > ArOH	Hydrophobic; PAC of no assistance	Lin <i>et al.</i> 2001
UF, hydrophilic	Cellulose acetate	Lake water; soil-derived humic acid	High MW hydrophobic acids	Only hydrophilic tested	Chang and Benjamin 1996; Gu <i>et al.</i> 1995
UF disc membranes, hydrophilic	Regenerated cellulose, cellulose diacetate	Suwannee River humic acid; BSA	Humic acid > protein since easier pore entry	Similar performance for all	Jones and O'Melia 2001
UF, both hydrophobic & hydrophilic	Polysulphone, acrylic copolymer, cellulosic	Lake Decatur, Illinois	Not determined	Hydrophobic	Laîné <i>et al.</i> 1989
UF and NF membranes, both hydrophobic & hydrophilic	Polyamide, PES, sulphonated PES, polysulphone, cellulose acetate, regenerated cellulose	Various surface supplies in California and Japan	Neutral hydrophilics a major foulant, except for very hydrophobic NOM	Hydrophobic membranes adsorbed more humic acids	Amy <i>et al.</i> 2001; Kimura <i>et al.</i> 2004
NF, of varying hydrophilicity	Thin film composite, cellulose acetate	Suwannee River, and Australian Dam	Humic acid > fulvic acid especially at high [Ca ⁺⁺]	Hydrophobic	Schäfer <i>et al.</i> 1998
NF, hydrophobic	Polysulphone	Fractionated Tar River, N. Carolina	Hydrophobic compounds	Only one tested	Nilson and DiGiano 1996

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407 Table 2

408 Amount of each NOM fraction in Meredith and Bendigo waters

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NOM	% TOC in each Fraction					
Source	SHA	WHA	Char	Neut	Res	HB
Meredith	43.8	21.9	19.2	15.3	15.1	0.2
Bendigo	38.6	26.0	19.3	16.1	15.7	0.4

410

411 **Table 3**

412 **The effect of Bendigo NOM fractions on flux, DOC 3.8 mg/L, 3 L throughput**

413

Membrane	Relative Flux							
	Raw	SHA	WHA	SHA + WHA	HA	Char	Neut	HB
PP	0.3	0.5	0.7	0.5	0.7	0.5	0.3	0.3
	0.3*	0.7*	0.8*	0.6*	-	0.6*	0.5*	0.5*
PVDF-1	-	0.2	0.3	0.3	-	-	-	-
	0.09 *	0.2*	0.4*	0.2*	-	0.3*	0.1*	-
PVDF-2	0.3	0.7	0.8	0.8	-	0.8	-	-
	0.6*	0.6*	0.9*	0.9*	-	0.9*	0.2*	-
PES-2	0.1	0.3	0.3	0.2	-	-	-	-
	0.2*	0.4*	0.5*	0.3*	-	0.2*	0.08 *	-

414 * At 1 L throughput

415

Table 4

The effect of NOM fractions on flux, with and without added salts, DOC 3 mg/l, 1.5 L throughput

Membrane	Added Salts*	Relative Flux					
		Raw	SHA	WHA	HA	Char	Neut**
PP	N	0.12	0.22	0.32	0.45	0.07	0.07
	Y	0.12	0.21	0.10	0.42	0.31	0.19
PVDF-2	N	0.48	0.75	0.77	0.97	0.74	0.45
	Y	0.72	0.65	0.85	0.94	0.57	0.60

* Final concentration 50 mg/L NaCl and 5 mg/L CaCl₂

** Type B, containing hydrophobic bases as well

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Fig. 1 Bendigo NOM fractions and PP membrane (p. 19)

Fig. 2 Meredith NOM fractions and PP membrane (p. 20)

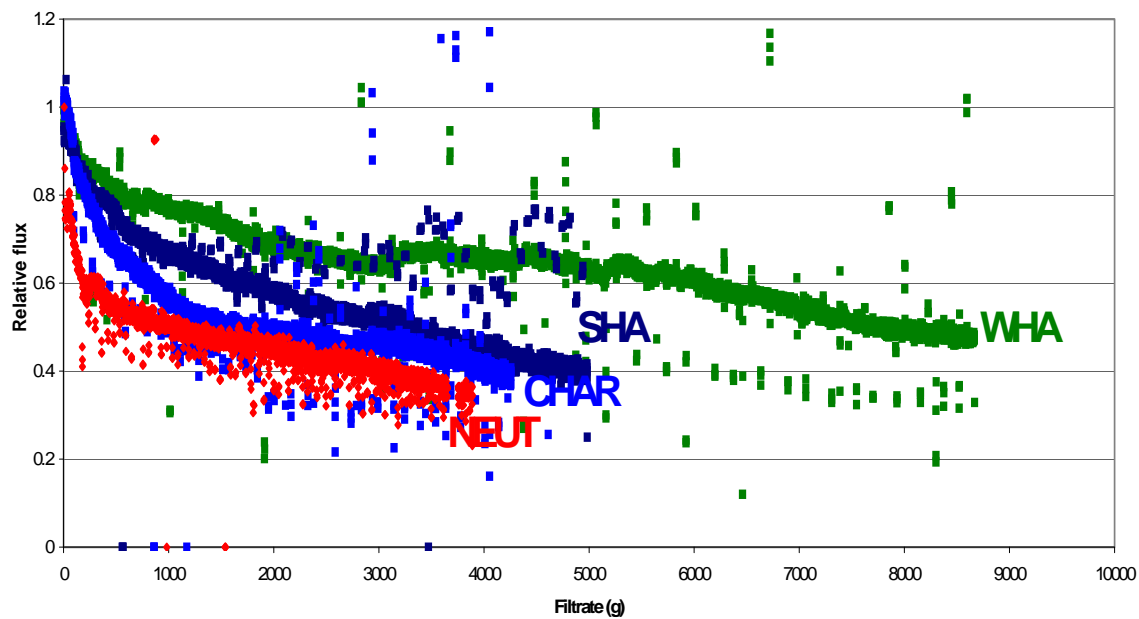
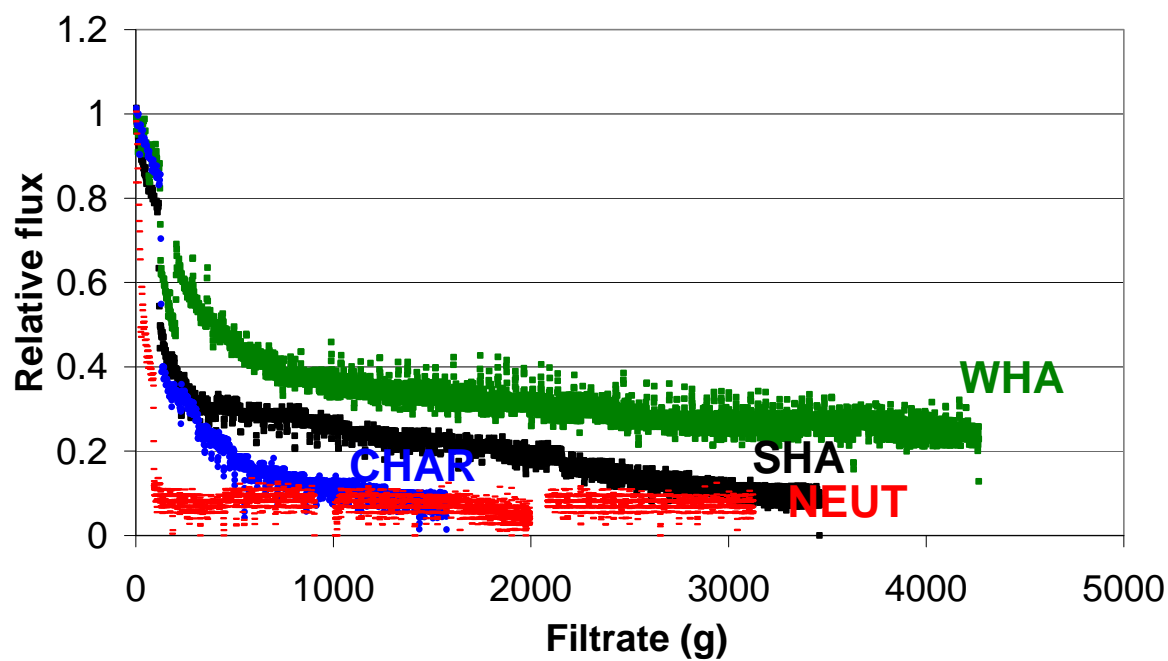


Fig. 1 Bendigo NOM fractions and PP membrane (p. 19)

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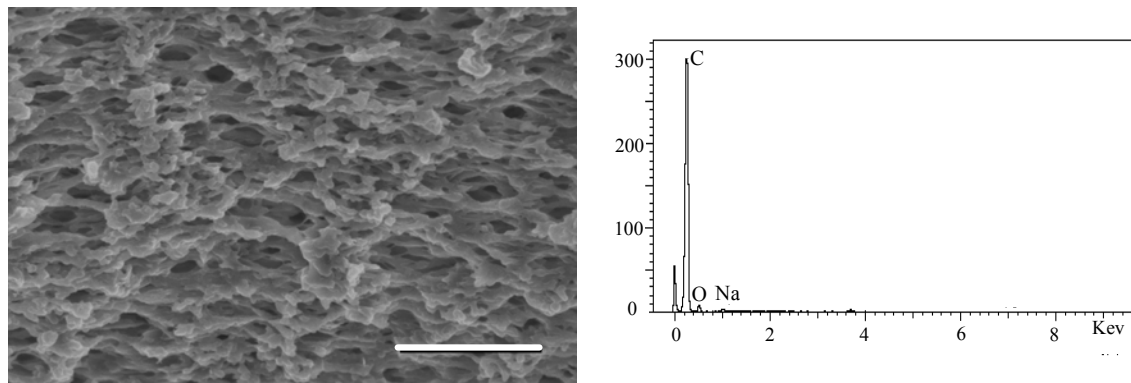
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446 Fig. 2 Meredith NOM fractions and PP membrane.

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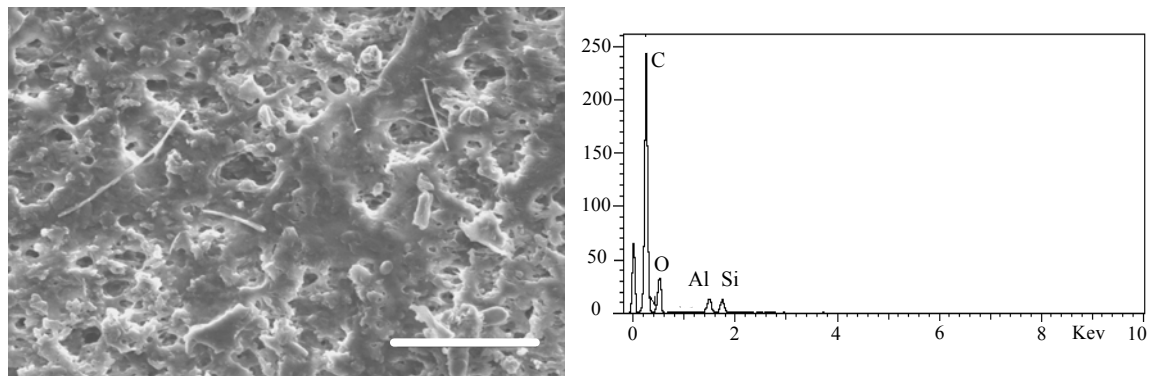


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451 **Figure 3:** SEM micrograph (bar = 5 μm) and EDS spectrum of a fresh PP membrane, showing
452 mostly carbon and some oxygen.

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Figure 4: SEM micrograph (bar = 10 μm) and EDS spectrum of a PP membrane following filtration of raw Meredith water, showing higher levels of oxygen, aluminium and silicon than those on fresh PP membrane.

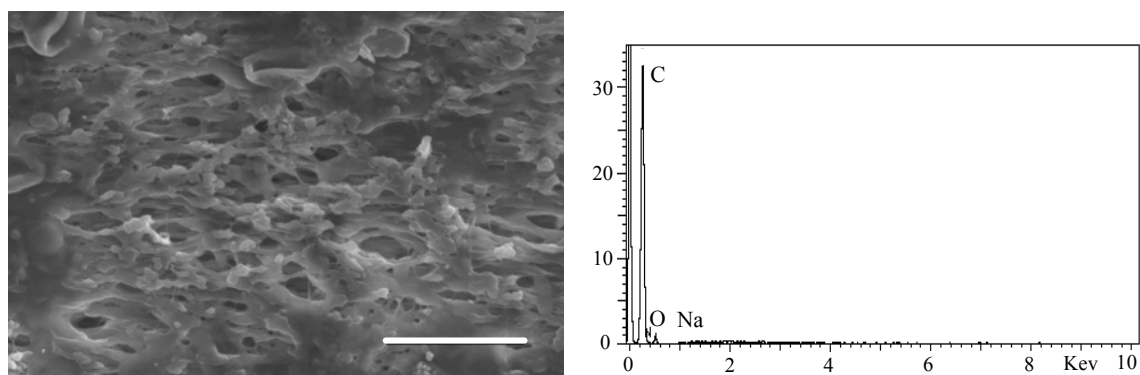
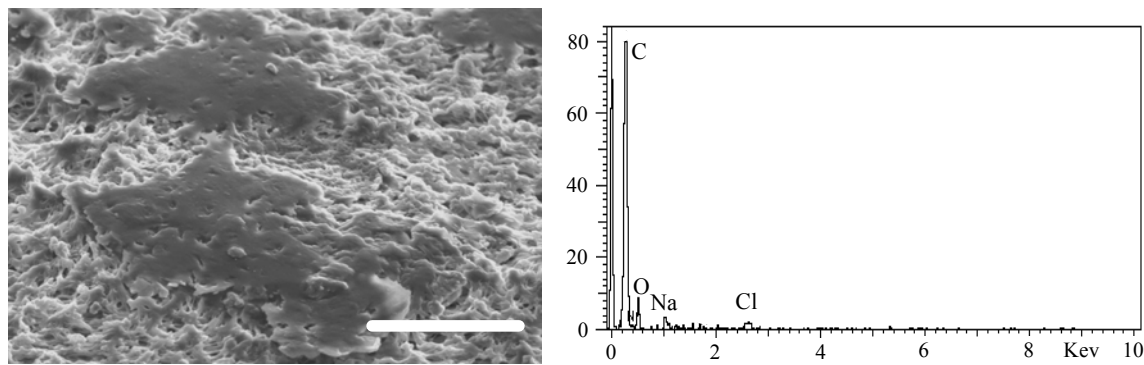


Figure 5: SEM micrograph (bar = 5 μm) and EDS spectrum of a PP membrane following filtration of the Meredith WHA fraction.

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473 **Figure 6:** SEM micrograph (bar = 10 μm) of a PP membrane following filtration of the Meredith
474 Char fraction showing discrete surface patches and aggregation of small particulate matter.
475 Corresponding EDS spectrum shows mostly carbon, oxygen, some sodium and chlorine.
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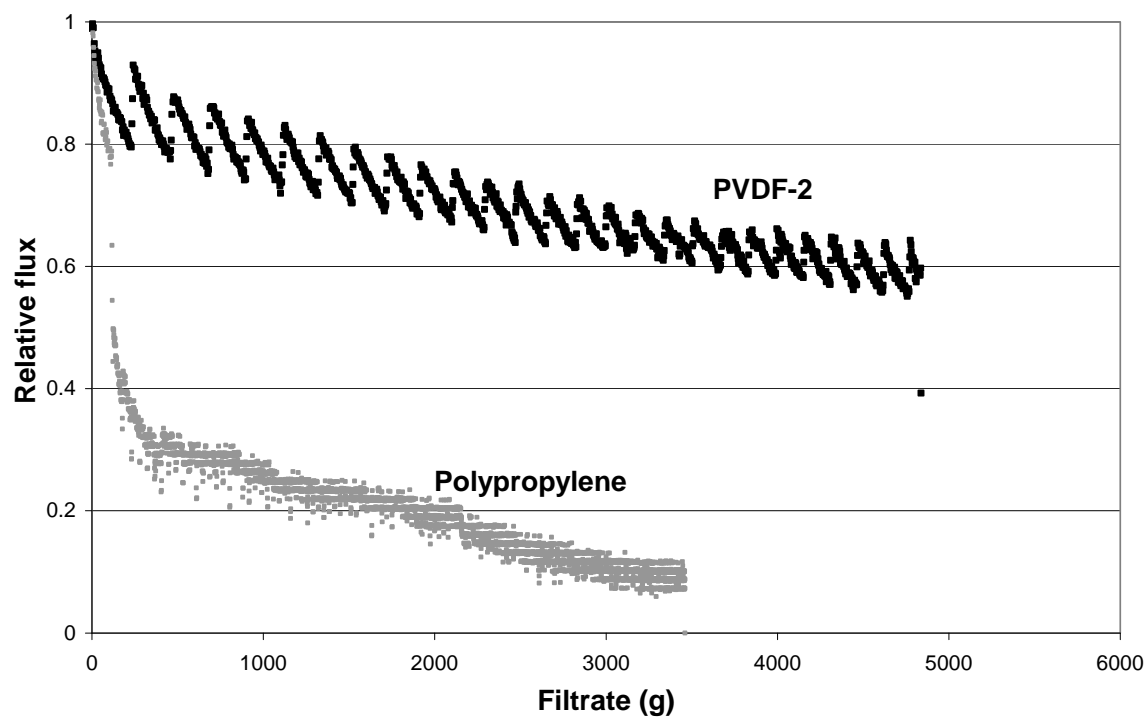


Fig. 7 Meredith NOM SHA fraction filtered through a PP and PVDF-2 membranes. Flux recovery on backwashing is indicated by the width of the lines.

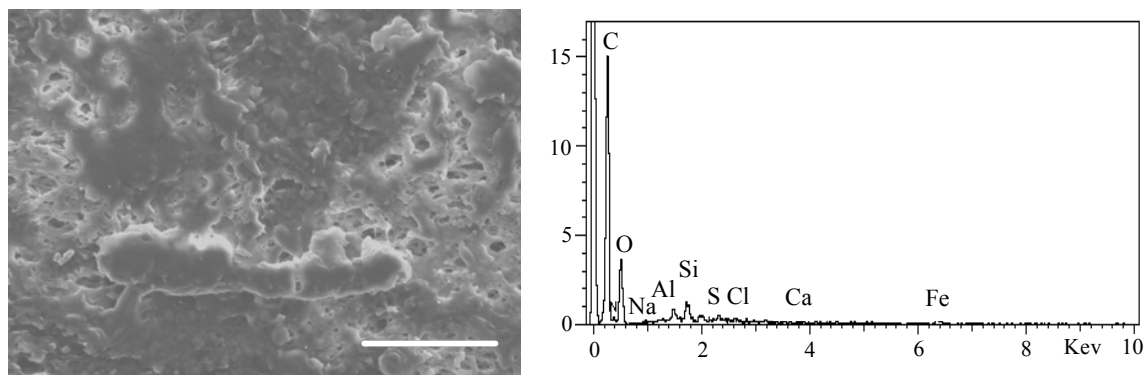


Figure 8: SEM micrograph (bar = 10 μm) and EDS spectrum of a PP membrane following filtration of the Meredith WHA fraction with salt addition (50mg/L NaCl and 5 mg/L CaCl_2). Note that addition of salt to WHA fraction caused 3-fold reduction in flux.